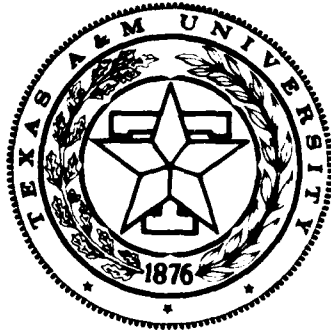


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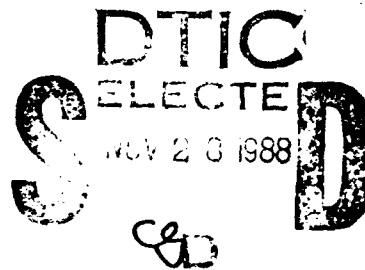
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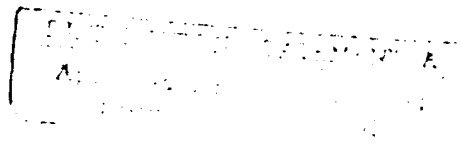
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A CONTINUUM DIFFUSION MODEL FOR VISCOELASTIC MATERIALS

Y. WEITSMAN



OFFICE OF NAVAL RESEARCH  
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## A CONTINUUM DIFFUSION MODEL FOR VISCOELASTIC MATERIALS

By

Y. Weitsman

Mechanics and Materials Center, Civil Engineering Department

Texas A&M University, College Station, Texas 77843-3136

## Abstract

A model for diffusion in polymers is established from basic principles of irreversible thermodynamics, employing the methodology of continuum mechanics. The polymeric materials are considered to respond viscoelastically, with ageing.

It is shown that effects of stress on diffusion and certain anomalies in the moisture sorption process can be explained by the present model.



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## 1. Introduction

The processes of moisture transport and sorption in polymers have been studied by numerous investigators for more than fifty years. Most of these studies, which involved experimental, analytical, and materials science aspects, were conducted by researchers in the fields of physical and polymer chemistry. These investigations were mostly focused towards applications in membrane technology and therefore concerned aspects of permeability and seepage. It is far beyond the scope of the present article to list the many significant contributions made to this field. References [1] - [9] list some of the many outstanding review articles on the subject.

During the past fifteen years the transport of moisture in polymers raised concern and interest in composite materials technology. Moisture plays a significant role in affecting the mechanical response of fiber-reinforced polymeric composites and in influencing the behavior of adhesive joints which are increasingly employed in composite structures. These concerns, which focus mainly on mechanical effects, produced more than 500 publications on the subject. A review and summary of some of these works is given in references [10] and [11].

In spite of many overlaps the investigations in the two foregoing categories reveal distinctions that reflect the disparate scientific disciplines from which they derive - polymer science in one case and applied mechanics in the other. It may thus be worthwhile to present an approach to theory of diffusion that employs the methodology of continuum mechanics and its well developed constitutive formalism. This approach is especially useful in the modelling of coupling effects, such as between stress and diffusion, as detailed in a recent work<sup>[12]</sup>.

It should be noted that the most crucial issue associated with diffusing

substances in polymeric composites is their detrimental effects on structural strength, integrity and durability. In certain circumstances, diffusing substances were noted to damage the composites by debonding the fiber/matrix interfaces. This issue is a topic of current research and its modelling is hampered by uncertainties regarding the damage mechanisms. Several investigations concerning moisture induced damage in composites were reviewed in ref. [11] and an attempt at a continuum-level modelling of the phenomenon is provided in ref. [13]. The issue of damage will not be discussed in the present paper.

## 2. Basic Equations

Consider a solid body  $B$  occupying a material volume  $V$  bounded by a surface  $A$ . Let the solid, of mass density  $\rho_s$ , absorb vapor through its boundary and let  $m$  denote the vapor-mass per unit volume of the solid. Also, let  $\underline{x}$  be the position of a solid mass particle in the deformed configuration that corresponds to the place  $\underline{X}$  in the undeformed state, and let  $\underline{f}$ ,  $\underline{g}$  and  $\underline{v}$  denote fluxes of vapor-mass and of heat, and the velocity of the solid particles, respectively.

In addition, let  $u$  and  $s$  be the internal energy and entropy densities of the solid/vapor mixture per unit solid mass, and let  $\sigma_{ij}$  and  $T$  denote the components of the Cauchy stress due to mechanically applied loads, and temperature, respectively.

A proper accounting of the state of the solid/vapor mixture, which is a thermodynamically open system, is obtained by considering each element in thermodynamic equilibrium with a reservoir containing vapor at pressure  $\tilde{p}$ , density  $\tilde{\rho}$ , and internal energy and entropy densities  $\tilde{u}$  and  $\tilde{s}$  respectively [14], [15], [16].

Conservation of the solid and vapor masses gives

$$\dot{\rho}_S + \rho_S \nabla \cdot \underline{v} = 0 \quad (1)$$

$$\dot{\underline{m}} = -\nabla \cdot \underline{f} \quad (2)$$

Conservation of energy over B reads

$$\begin{aligned} \frac{d}{dt} \int_V \rho_S u \, dV = & \int_A \sigma_{ij} n_j v_i \, dA - \int_A q_i n_i \, dA \\ & - \int_A \tilde{p} \frac{f_i}{\tilde{\rho}} n_i \, dA - \int_A \tilde{u} f_i n_i \, dA \end{aligned} \quad (3)$$

The third integral on the right side of (3) expresses the mechanical power due to vapor flux, observing that  $f_i/\tilde{\rho}$  corresponds to vapor velocity. The last integral in (3) expresses the rate of vapor-borne energy.

The entropy inequality reads

$$\frac{d}{dt} \int_V \rho_S s \, dV \geq \int_A -(q_i/T) n_i \, dA - \int_A \tilde{s} f_i n_i \, dA \quad (4)$$

Where the last integral in (4) expresses the rate of vapor-borne entropy.

Application of Green's theorem to (3) and (4), and employment of (2), yields [12]

$$\rho_S \dot{\underline{u}} = \sigma_{ij} v_{i,j} - q_{i,i} - \tilde{h}_{,i} f_i + \tilde{h} \dot{\underline{m}} \quad (5)$$

and

$$\rho_S T \dot{\underline{s}} \geq -q_{i,i} + (q_i/T) g_i - T \tilde{s}_{,i} f_i + T \tilde{s} \dot{\underline{m}} \quad (6)$$

where  $\tilde{h} = (\tilde{p}/\tilde{\rho}) + \tilde{u}$  is the enthalpy of the vapor in the hypothetical reservoir and  $g_i = T_{,i}$ .

Elimination of  $q_{i,i}$  between (5) and (6) yields the following expression for the "reduced entropy inequality" [12]

$$-\rho_{so}\dot{\phi} - \rho_{so}s\dot{T} - \dot{\epsilon}_{ij}\epsilon_{ij} - (q_i/T)g_i + \tilde{p}\dot{m} - f_{ij}\tilde{p}_{,i} - \tilde{s}g_if_i \geq 0 \quad (7)$$

In (7)  $\phi = u - Ts - \frac{1}{\rho_{so}}\epsilon_{ij}\epsilon_{ij}$  is the Gibbs free energy and  $\tilde{p} = \tilde{h} - T\tilde{s}$  is the chemical potential of the vapor in the hypothetical reservoir. In eqn. (7)  $\rho_{so}$  denotes the initial mass density of the solid and infinitesimal deformation has been assumed, whereby  $\epsilon_{ij} \ll 1$ .

### 3. Ageing Viscoelastic Response With Moisture.

The viscoelastic behavior of high polymers has been associated with the various degrees of freedom afforded by the motions of the long chain molecules [17], [18], [19]. The normal modes of these motions can be represented by  $N$  scalar-valued internal state variables  $\gamma_r$  ( $r = 1, \dots, N$ ). This representation motivated subsequent researchers [20]-[24] to derive a theory of viscoelasticity from fundamental concepts of irreversible thermodynamics, with irreversibility stemming from the foregoing variables  $\gamma_r$  through "growth laws" that correspond to viscous resistance.

The physical ageing of polymers is generally ascribed [24] to the introduction of a "free volume" into those materials upon their cooling across the glass transition temperature  $T_g$ . The free volume is a non-equilibrium thermodynamic internal state variable, which decays spontaneously with the passage of time and influences the rate of all time-dependent processes within the polymer.

Consider therefore

$$\phi = \phi(\sigma_{ij}, m, T, \gamma_r, v_f) \quad (8)$$

where  $v_f$  denotes the non-dimensional free-volume fraction.

Since eqn. (7) cannot be violated by any process, the methodology of continuum mechanics [26] yields the following constitutive equations

$$\begin{aligned}\epsilon_{ij} &= -\rho_{so} \frac{\partial \phi}{\partial \sigma_{ij}} \\ s &= -\frac{\partial \phi}{\partial T} \\ \mu &= \rho_{so} \frac{\partial \phi}{\partial m}\end{aligned}\quad (9)$$

and

$$-R_r \dot{\gamma}_r - R \dot{v}_f - (q_i/T)g_i - \tilde{s} g_i f_i \geq 0 \quad (10)$$

In eqn. (10), the affinities  $R_r$  and  $R$  are defined by

$$R_r = \rho_{so} \frac{\partial \phi}{\partial \gamma_r} \quad \text{and} \quad R = \rho_{so} \frac{\partial \phi}{\partial v_f}.$$

The aging process is associated with the spontaneous collapse of the free volume  $v_f$  [25],[27] from an initial value  $v_{f0}$ , which is created by the cooling of a polymer across its glass transition temperature  $T_g$  down to a temperature  $T_0$ . In addition, the subjection of a polymer externally to  $\sigma_{ij}$ ,  $m$ , or  $\Delta T = T - T_0$ , will trigger an irreversible process which will cause the internal variables  $\gamma_r$  to drift spontaneously toward their equilibrium values  $\gamma_r^e$ . The two abovementioned processes are assumed independent of each other [25],[27]. Consequently, while both  $\dot{\gamma}_r$  and  $\dot{v}_f$  in eqn. (10) denote derivatives with respect to time, the time-lapse  $t$  for  $\gamma_r$  is not necessarily equal to the time-span  $\tau$  for  $v_f$ .

Assume  $\gamma_r, v_f \ll 1$ . A Taylor expansion about the initial state ( $\gamma_r = 0, v_f = v_{f0}$ ) then reads

$$\begin{aligned}\rho_{so}\phi &= \rho_{so}[\phi_0 + \phi_r \gamma_r + \phi_v (v_f - v_{f0}) + \frac{1}{2} \phi_{rq} \gamma_r \gamma_q + \frac{1}{2} \phi_{vv} (v_f - v_{f0})^2 \\ &\quad + \text{H.O.T.}] \end{aligned} \quad (12)$$

In eqn. (12)  $\phi_0 = \phi_0(\sigma_{ij}, m, T, 0, v_{f0})$  and  $\phi_r, \phi_v, \phi_{rq}, \phi_{vv}$  denote partial



derivatives at  $\gamma_r = 0$ ,  $v_f = v_{f0}$ , all of which depend on  $\sigma_{ij}$ ,  $m$ , and  $T$ .

According to the extremum principles of thermodynamics<sup>[28]</sup>  $\phi$  attains its minimum at the equilibrium values  $\gamma_r = \gamma_r^e$  and  $v_f = v_f^e$ . Therefore, at equilibrium we have

$$\frac{\partial \phi}{\partial \gamma_r} = 0, \quad \frac{\partial \phi}{\partial v_f} = 0, \quad \text{and}$$

$$\frac{1}{2} \frac{\partial^2 \phi}{\partial \gamma_r \partial \gamma_s} \delta \gamma_r \delta \gamma_s + \frac{1}{2} \frac{\partial^2 \phi}{\partial v_f^2} (\delta v_f)^2 > 0 \quad \text{for all } \delta \gamma_r \text{ and } \delta v_f.$$

Expanding  $\phi$  about  $\gamma_r^e$  and  $v_f^e = 0$  we have

$$\rho_{so} \phi = \rho_{so} [\phi_e + \frac{1}{2} \phi_{rq}^e (\gamma_r - \gamma_r^e) (\gamma_q - \gamma_q^e) + \frac{1}{2} \phi_{vv}^e v_f^2 + \text{H.O.T.}] \quad (13)$$

In view of the assumption that  $\gamma_r, \gamma_r^e, v_f, v_{f0} \ll 1$ , expansions (12) and (13) are equal, implying in particular that

$$\phi_{vv} = \phi_{vv}^e, \quad \phi_{rq} = \phi_{rq}^e.$$

Therefore,  $\phi_{vv} > 0$  and  $\phi_{rq}$  are components of a symmetric, positive definite matrix.

Employing the familiar assumption of viscous-like resistance<sup>[17]-[23]</sup> let

$$R = -b(m, T, v_f) \frac{dv_f}{d\tau} \quad (14)$$

and

$$R_r = -b_{rq}(m, T, v_f) \frac{d\gamma_q}{dt} \quad (15)$$

By Onsager's principle  $b_{rq} = b_{qr}$  and, in view of the dissipation inequality (10),  $b > 0$  and  $b_{rq}$  are components of a semi positive definite, symmetric matrix. As noted earlier, the time  $\tau$  and  $t$  in eqns. (14) and (15) are distinct because the quench-time  $\tau$  usually occurs earlier than the exposure-time  $t$ , namely  $t = \tau - t_e$ .

Equations (11), (13) and (14) give

$$\rho_{so} \ddot{\gamma}_{vv}^e v_f + b \frac{dv_f}{d\tau} = 0 \quad (16)$$

whereby

$$v_f = v_{fo} e^{-\xi/\tau_v} \quad (17)$$

with  $d\xi = d\tau/b$  and  $\tau_v^{-1} = \rho_{so} \ddot{\gamma}_{vv}^e$

Equations (11), (12) and (15) yield

$$\rho_{so} \ddot{\gamma}_{rq} + b_{rq} \dot{\gamma}_q = -\rho_{so} \ddot{\gamma}_r \quad (18)$$

Since  $\ddot{\gamma}_{rq}$  and  $b_{rq}$  are symmetric, positive definite matrices\* they can be diagonalized simultaneously [29] and eqn. (18) is expressible in the form

$$\rho_{so} \ddot{\gamma}_p + B_p \dot{\gamma}_p = -\rho_{so} \ddot{\gamma}_p \quad (p = 1, \dots, N. \text{ no sum on } p) \quad (19)$$

Note that  $b_{rq}$ , and therefore also  $B_p$ , depend on the quency-time  $\tau$  as well as on the exposure-time  $t$  through their dependence on  $m$ ,  $T$  and  $v_f$  in eqn. (15).

Following Schapery [22]-[24] assume that all  $\ddot{\gamma}_{rq}$  have a common dependence on  $\sigma_{ij}$ ,  $m$ , and  $T$  namely  $\ddot{\gamma}_{rq} = a_G(\sigma_{ij}, m, T) \phi_{rq}^0$  with constant  $\phi_{rq}^0$  and, similarly,  $b_{rq} = a(m, T, v_f) b_{rq}^0$ . These common "shift-factors"  $a_G$  and  $a$  carry over to eqn. (19) whose solution, subject to the conditions  $\gamma_r(0) = 0$ ,  $\gamma_r(\infty) = \gamma_r^e$ , reads

$$\hat{\gamma}_p = -K_p (1 - e^{-\xi/\tau_p}) \quad (20)$$

\*The case of a semi-positive definite  $b_{rq}$  is omitted here for the sake of brevity. This case corresponds to a viscoelastic fluid, as modelled by a free dash pot attached to Kelvin or Maxwell elements.

where

$$\kappa_p = \frac{\phi_p}{a_G \phi_p}, \quad \tau_p = \frac{B_p}{\rho_{so} \phi_p} \quad (\text{no sum on } p, p = 1, 2, \dots, N) \quad (21)$$

and

$$d\xi = \left(\frac{a_G}{a}\right) dt. \quad (22)$$

Aiming at linear stress-strain behavior, consider  $\sigma_{ij}/E \ll 1$  where  $E$  denotes a characteristic modulus. To retain linearity assume that all retardation times do not depend on  $\sigma_{ij}$ . Hence, in eqns. (17) and (20),  $\tau_v = \tau_v(m, T, v_f)$  and  $\tau_p = \tau_p(m, T, v_f)$   $p = 1, \dots, N$ . Furthermore, to establish the linear stress-strain relations, consider the expansion in eqn. (12) truncated after three-terms, which, resorting to the diagonalized form, reads

$$\rho_{so} \phi = \rho_{so} [\phi_0 + \phi_r \hat{\gamma}_r + \phi_v (v_f - v_{f0})] \quad (23)$$

Eqn. (9)<sub>1</sub> gives

$$\epsilon_{ij} = -\rho_{so} \left[ \frac{\partial \phi_0}{\partial \sigma_{ij}} + \frac{\partial \phi_r}{\partial \sigma_{ij}} \hat{\gamma}_r + \frac{\partial \phi_v}{\partial \sigma_{ij}} (v_f - v_{f0}) \right] \quad (24)$$

The specific forms which follow from eqn. (24) depend on the material symmetry at hand. Considering isotropy we have

$$\phi(\sigma_{ij}, m, T, \hat{\gamma}_r, v_f) = \phi(\sigma_{kk}, \sigma_{ij} \sigma_{ij}, m, T, \hat{\gamma}_r, v_f)^*$$

which, for linear behavior gives the well known forms

$$\begin{aligned} \rho_{so} \phi_0 &= A_0(m, T) - L_0(m, T) \sigma_{kk} - M_0(m, T) \sigma_{kk} \sigma_{\ell\ell} - N_0(m, T) \sigma_{k\ell} \sigma_{\ell k} \\ \rho_{so} \phi_r &= A_r(m, T) + L_r(m, T) \sigma_{kk} + M_r(m, T) \sigma_{kk} \sigma_{\ell\ell} + N_r(m, T) \sigma_{k\ell} \sigma_{\ell k} \\ \rho_{so} \phi_v &= A_v(m, T) + L_v(m, T) \sigma_{kk} + M_v(m, T) \sigma_{kk} \sigma_{\ell\ell} + N_v(m, T) \sigma_{k\ell} \sigma_{\ell k} \end{aligned} \quad (25)$$

It is advantageous to express  $L_0$ ,  $L_r$  and  $L_v$  in terms of expansional coefficients  $\alpha$  and  $\beta$ , namely

\*The stress invariant  $|\sigma_{ij}|$  is inadmissible for linear behavior.

$$L(m, T) = \alpha(m, T)\Delta T + \beta(m, T)m \quad (26)$$

Equations (24) and (25) then yield

$$\begin{aligned} \epsilon_{ij} = & [\hat{\alpha}_0 - \hat{\alpha}_r \hat{\gamma}_r - \hat{\alpha}_v(v_f - v_{f0})]\Delta T \delta_{ij} + [\hat{\beta}_0 - \hat{\beta}_r \hat{\gamma}_r - \hat{\beta}_v(v_f - v_{f0})]m \delta_{ij} \\ & + 2[M_0 - M_r \hat{\gamma}_r - M_v(v_f - v_{f0})]\sigma_{kk} \delta_{ij} + 2[N_0 - N_r \hat{\gamma}_r - N_v(v_f - v_{f0})]\sigma_{ij} \end{aligned} \quad (27)$$

It can be noted from eqns. (20) and (21) that  $\gamma_p$  depends on  $\sigma_{ij}$  through the presence of  $\phi_p$  in  $K_p$ . However, for sufficiently small stresses  $K_p$  themselves can be expanded according to (25), whereby upon collecting like-powers in  $\sigma_{ij}$ , the form of the strain-stress relationship given in eqn. (27) remains valid with stress-independent  $\hat{\gamma}_r$ .

The stress strain relations (27) are of the familiar form employed in linear viscoelasticity, except that the retardation spectra incorporate now ageing effects and all instantaneous compliances age with time. Recalling eqn (20), for a discrete spectrum of retardation-times  $\tau_r$  expressions (27) read

$$\begin{aligned} \epsilon_{ij} = & [\alpha_0 + \alpha_1(1-e^{-\xi/\tau_v}) + \sum_r \alpha_r(1-e^{-\xi/\tau_r})]\Delta T \\ & + [\beta_0 + \beta_1(1-e^{-\xi/\tau_v}) + \sum_r \beta_r(1-e^{-\xi/\tau_r})]m \\ & + [B_0 + B_1(1-e^{-\xi/\tau_v}) + \sum_r B_r(1-e^{-\xi/\tau_r})]\sigma_{kk} \delta_{ij} \\ & + [J_0 + J_1(1-e^{-\xi/\tau_v}) + \sum_r J_r(1-e^{-\xi/\tau_r})]\sigma_{ij} \end{aligned} \quad (28)$$

In eqn. (28), the quantities  $\alpha$ ,  $\beta$ ,  $B$  and  $J$  depend on  $m$  and  $T$ , the "reduced times"  $\xi$  and  $\zeta$  both depend on  $m$ ,  $T$  and the ageing time  $\tau$ . However, in contrast to  $\zeta$ , the reduced time  $\xi$  is measured from the time of application of  $\sigma_{ij}$ ,  $m$ , and  $T$ . For fluctuating environments and stresses, expression (28) takes the form of convolution integrals. The case of a continuous spectrum of retardation times  $\tau_r$  can be represented in the familiar manner by means of retardation integrals.

#### 4. Stress Assisted Diffusion in Ageing Viscoelastic Media

Employing eqns. (9)<sub>3</sub>, (23), (25) and (26) we obtain

$$\begin{aligned}
 \mu = & \frac{\partial A_0}{\partial m} + \frac{\partial A_r(m,T)}{\partial m} \gamma_r + \frac{\partial A_v(m,T)}{\partial m} (v_f - v_{f0}) \\
 & + \left\{ \left[ -\frac{\partial \alpha_0}{\partial m} + \frac{\partial \alpha_r}{\partial m} \gamma_r + \frac{\partial \alpha_v}{\partial m} (v_f - v_{f0}) \right] \Delta T \right. \\
 & \quad \left. - \frac{\partial (m\beta_0)}{\partial m} + \frac{\partial (m\beta_r)}{\partial m} \gamma_r + \frac{\partial (m\beta_v)}{\partial m} (v_f - v_{f0}) \right\} \sigma_{kk} \\
 & + \left[ -\frac{\partial M_0}{\partial m} + \frac{\partial M_r}{\partial m} \gamma_r + \frac{\partial M_v}{\partial m} (v_f - v_{f0}) \right] \sigma_{kk} \sigma_{\ell\ell} \\
 & + \left[ -\frac{\partial N_0}{\partial m} + \frac{\partial N_r}{\partial m} \gamma_r + \frac{\partial N_v}{\partial m} (v_f - v_{f0}) \right] \sigma_{k\ell} \sigma_{\ell k}
 \end{aligned} \quad (29)$$

The boundary conditions for moisture transport are

$$\mu(x,t) = \mu_A(x,t) \quad \underline{x} \text{ on boundary} \quad (30)$$

where  $\mu_A$  represents the chemical potential of the ambient vapor.

Assume for simplicity that the expansional coefficients  $\alpha$  and  $\beta$  do not vary with  $m$ . In this case eqns. (29) and (30), together with eqn. (20), yield

$$\begin{aligned}
 \frac{\partial A_0}{\partial m} = & \mu_A + \sum_r W_r(m,T) (1 - e^{-\xi/\tau_r}) + W(m,T) (1 - e^{-\xi/\tau_v}) \\
 & + \left[ -\beta_0 + \sum_r \beta_r (1 - e^{-\xi/\tau_r}) + \beta_v (1 - e^{-\xi/\tau_v}) \right] \sigma_{kk} \\
 & + \left[ -Y(m,T) + \sum_r Y_r(m,T) (1 - e^{-\xi/\tau_r}) + Y_v (1 - e^{-\xi/\tau_v}) \right] \sigma_{kk} \sigma_{\ell\ell} \\
 & + \left[ -Z(m,T) + \sum_r Z_r(m,T) (1 - e^{-\xi/\tau_r}) + Z_v (1 - e^{-\xi/\tau_v}) \right] \sigma_{k\ell} \sigma_{\ell k}
 \end{aligned} \quad (31)$$

Eqn. (31) illuminates the effects of viscoelastic retardation and ageing, as well as of stress, on the diffusion process. In the absence of those effects the boundary condition, which reads  $\partial A_0/\partial m = \mu_A$ , translates into the familiar statement  $m(\underline{x},t) = m_0(t)$ ,  $\underline{x}$  on boundary and  $m_0$  prescribed. In contrast, eqn. (31) states that the equilibrium boundary value is approached

gradually with time (even for exposure to constant ambient vapor pressure), it is affected by age, and depends quadratically on the applied stress.

Consider now the diffusion coefficient  $D$ . Since this coefficient reflects micro-level phenomena, its form cannot be derived from a continuum model\*. Molecular-level considerations of diffusion in solids<sup>[30]</sup> and fluids<sup>[31]</sup> suggest that

$D \sim \text{Vacancy in host material} \cdot \text{Agitation energy of diffusing substance}$

In the present case it is reasonable to expect that the vacancy would depend mostly on  $v_f$  and secondarily on  $m, T$  and  $\sigma_{ij}$  (through their influence on swelling strains). On the other hand, the agitation energy would depend mostly on  $T$ .

Accordingly

$$D \sim D_0[m, T, v_f(\xi(\tau)), \int_0^t F(\xi(t) - \xi(\tau)) \frac{d\sigma_{kk}}{d\tau} d\tau] \cdot (\exp(-E/RT)) \quad (32)$$

In the absence of a satisfactory molecular theory for the glassy state at the present time it appears expedient to base the form of  $D$  on empirical evidence.

In isotropic materials, the flux of moisture at fixed  $\sigma_{ij}$  and  $T$  is taken to be\*\*

$$f_i = -D \frac{\partial \mu}{\partial x_i} \quad (33)$$

Consequently, eqn. (2) yields the field equation

\*The principle of equi-presence suggests that  $D = D(\sigma_{ij}, m, T, \gamma_r, v_f)$  but provides no further insight.

\*\*When  $m, T$  and  $\sigma_{ij}$  vary in space couplings occur between the fluxes of moisture and of temperature and both depend on the gradients of  $\mu, T$ <sup>[32]</sup> and of the invariants of stress <sup>[12]</sup>.

$$\frac{\partial m}{\partial t} = \frac{\partial}{\partial x_i} \left( D \frac{\partial m}{\partial x_i} \right) \quad (34)$$

In view of eqns. (29) and (32), relations (33) and (34) are extremely complicated even at  $T = T_0$  and  $\sigma_{ij} = \sigma_{ij}^0$ . the complexity is due to the presence of  $m$  in  $D$  and  $v_f$  (through  $\xi(\tau)$ , and  $\zeta(\tau)$  in the compliances listed in eq. (29)). However, inspite of the cumbersome details and the paucity in information several features of the form of equation (34) emerge. Accordingly, the diffusion equation:

- (1) Contains non-linear terms in the moisture gradient  $\partial m / \partial x_i$ .
- (2) Follows a time-retardation process akin to mechanical viscoelastic response.
- (3) Varies non-linearly with external stresses  $\sigma_{ij}$ .
- (4) Exhibits an ageing behavior characteristic of glassy polymers.

### 5. Two-Phase Diffusion

The non-Fickian weight uptake of water vapor by epoxy resins can be described by a two-phase diffusion model. This model assumes that the vapor within the polymer divides into two portions - a bound phase  $m_c$  and a mobile phase  $m_a$ . Details are given in refs. [33], [34], where the resin's viscoelasticity has been discarded.

It is interesting to note that the above model can be derived in the context of the thermodynamic theory developed in this work. In this case, let

$$\rho_{SO} \phi = \rho_{SO} \phi (\sigma_{ij}, m_a, m_c, T, \gamma_r, v_f) \quad (35)$$

In analogy with sections 2-4 we now have

$$\mu_a = \rho_{SO} \frac{\partial \phi}{\partial m_a}, \quad \mu_c = \rho_{SO} \frac{\partial \phi}{\partial m_c}$$

Equation (29) and the boundary condition (31) pertain now to the chemical

potential of the mobile phase  $\mu_a$ , so that all partial derivatives in those equations should be taken with respect to  $m_a$  instead of  $m$ .

Similarly, the flux-gradient relation now involves the mobile phase only, so that eqn. (33) is replaced by

$$f_i = -D \frac{\partial \mu_a}{\partial x_i} \quad (36)$$

Since the balance equation (2) remains valid, equation (34) is replaced now by

$$\frac{\partial (m_a + m_c)}{\partial t} = \frac{\partial}{\partial x_i} \left( D \frac{\partial \mu_a}{\partial x_i} \right) \quad (37)$$

The system of equations is supplemented by the phase interaction relation [33], [34]

$$\frac{\partial m_c}{\partial t} = P m_c - Q m_a \quad (38)$$

where  $P$  and  $Q$  are empirical factors.

The dependence of field equations and boundary conditions on retardation-times, physical ageing and stress is retained for the case of two-phase diffusion and is expressible in the same forms as presented in section 4.

## 6. Experimental Observations.

The present constitutive model can be employed to explain certain experimental observations on diffusion in polymers, as shown in Figs. 1-9 below.

Fig. 1 exhibits the uptake of water vapor, from an ambient environment maintained at a fixed level of 97% R.H., by unidirectionally reinforced graphite/epoxy coupons. The per-cent weight gain is plotted vs.  $\sqrt{\text{time}}$ . Note the discrepancy between data and predictions based upon the linear Fickian model.



On the other hand, when the retardation process of the epoxy is taken in consideration by means of a boundary condition of the form

$$m(\text{boundary}) = m_a + m_b (1 - e^{-t/\tau_1}) \quad (39)$$

it is possible to obtain an excellent fit between data and theory. In eqn. (39)  $m_a$  corresponds to the instantaneous response and  $m_b$  is the contribution of polymeric retardation processes. The corresponding prediction, with  $m_a = 1.2\%$ ,  $m_b = 0.467\%$ , and  $\tau_1 = 2.63 \times 10^6$  min., is drawn with a solid line in Fig. 1.\* It is worth noting that the above value of  $\tau_1$  falls roughly in the middle of the spectrum of mechanical retardation-times for epoxy.

Another form of history-dependence of moisture sorption in epoxy is suggested in Fig. 2<sup>[36]</sup>. According to those data there exists a distinct difference in the moisture up-take of "as prepared" samples and the re-absorption by saturated-and-dried samples. This behavior can be attributed to the possibility that re-absorption may have occurred before the complete recovery of the retardation processes caused by the earlier exposure.

It is possible to match data of the type shown in Figure 2 with the boundary condition expressed in eqn. (39). The incomplete viscoelastic recovery at the onset of the second exposure to moisture can be introduced by an enhanced value of  $m_a$ , compensated by a reduced value of  $m_b$ , maintaining  $m_a + m_b = m_\infty = \text{constant}$ . Alternately, the incomplete viscoelastic recovery may be expressed by an increased value of  $\tau_1$ . The trends are exhibited in Figs. 3 and 4 respectively.

Effects of stress on diffusion are shown in Figs. 5-8<sup>[37]-[39]</sup>. Fig. 5 shows the per-cent weight gain of water vapor, maintained at 97% R.H., by

\*An analytic solution for boundary condition (39) is available in Ref. [35].

epoxy coupons that were subjected to various levels of uniaxial tensile stress. The weight-gain is plotted vs.  $\sqrt{\text{time}}$  and data are compared against predictions of the linear Fickian law, showing discrepancies that increase with stress. The maximal level of moisture up-take reached during the tests (which lasted about seven weeks) are plotted vs. stress in Fig. 6. Although the above maximal levels of moisture uptake are not the equilibrium saturation levels, Fig. 6 shows a trend which suggests a quadratic relation between saturation levels and stress, as suggested in section 4.

In Figs. 5 and 6 the ultimate tensile stress was  $\sigma_{ult.} = 5.17 \text{ MPa}$ .

The dependence of water absorption by polymers on compressive stress levels was reported in ref. [38]. In particular, the sorption of distilled water by epoxy coupons subjected to uniaxial compression is shown in Fig. 7. In spite of the relatively short duration of these tests, which were terminated much below saturation, they indicate a non-linear relationship between stress and saturation levels.

A similar, though less direct, non-linear relation between stress and saturation levels is inferred from Fig. 8.<sup>[39]</sup> This figure shows the reduced permeability associated with the flow of oxygen gas across a membrane made of extruded PET, when the membrane is subjected to various levels of uniaxial and biaxial tensile stresses.

A more intricate kind of sorption behavior is shown in Fig. 9<sup>[36]</sup>. Since earlier experiments have shown that equilibrium solubility decrease with temperature<sup>[36]</sup>, one might expect to observe water desorption when a specimen equilibrated at 75°C is transferred to a water bath at 23°C. However, Fig. 9 shows that the opposite takes place. A similar phenomenon was also observed in graphite/epoxy composites<sup>[40]</sup>.

One possible explanation of this behavior, in addition to those suggested

in [36], is that the slow, decelerating collapse of the free volume (initiated when the sample was created) is reactivated in the saturated epoxy when it is cooled from 75°C down to 23°C. Indeed, it was indicated in [36], that for saturated epoxy  $T_g$  is lowered to 108°C. According to eqns. (29) and (30) the rejuvenation of the process of free volume collapse would indeed be reflected in an increased saturation level.

#### 6. Concluding Remarks

In this article it was shown that the constitutive formalism of continuum mechanics can be employed to model several aspects of the process of diffusion in polymers. Certain micro-level characteristics of the polymer structure, such as free volume and motion degrees-of-freedom, were incorporated as internal state variables. The constitutive formalism led to a linear viscoelastic model with ageing and resulted in diffusion relations that were coupled with stress and with the time-dependent material response.

On the other hand, it was shown that the continuum mechanics formalism provides only scant information about material parameters such as the diffusion coefficient. This shortcoming is attributable to the fact that continuum mechanics, which aims at the modelling of macro-level phenomena, is unsuitable for describing inherently micro-level aspects. This conclusion indicates that an interdisciplinary effort, combining continuum mechanics and polymer science, is required for a comprehensive formulation of the diffusion process.

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### Figure Titles

- Fig. 1: Moisture weight gain (%) in a 12-ply unidirectional AS4/3502 graphite/epoxy laminate under exposure to constant ambient relative humidity of 97%, Vs.  $\sqrt{\text{time}}$ . Temperature = 73°C. Data (dots), predictions of Fick's law (dashed line), and of eqn. (39) (solid line). Values of  $m_a$ ,  $m_b$  and  $\tau_1$  given in text.
- Fig. 2: Solubility  $S$  (in %) Vs. non-dimensional  $\sqrt{\text{time}}$  of epoxy samples immersed in water at 23°C. Open circles - samples as prepared, solid circles - samples previously swollen and dried. After Apicella et. al., reference [36].
- Fig. 3: Moisture weight gain (%) Vs.  $\sqrt{\text{time}}$  for test conditions as in Fig. 1 and predictions according to eqn. (39).  $m_a$  and  $m_b$  as in text (dashed line) and  $\bar{m}_a = 1.25 m_a$ ,  $\bar{m}_b = m_b - 0.25 m_a$  (solid line). In both cases  $\tau_1$  is same as in text.
- Fig. 4: Moisture weight gain (%) Vs.  $\sqrt{\text{time}}$  for test conditions as in Fig. 1 and predictions according to eqn. (39).  $\tau_1$  as in text (solid line) and  $\bar{\tau}_1 = \tau_1/2$  (dashed line). In both cases  $m_a$  and  $m_b$  are same as in text.
- Fig. 5: Average values of moisture weight gains (%) Vs.  $\sqrt{\text{time}}$  of 3502 epoxy coupons subjected to various stress levels under constant relative humidity of 97% and at temperature of 40°C. Predictions of Fick's law are drawn by dashed lines. After Henson and Weitsman, reference [37].
- Fig. 6: Maximal levels of moisture weight gain (%) attained in 3502 epoxy samples after five weeks of exposure to humidity under various stress levels. Conditions same as in Fig. 5. After Henson and Weitsman, reference [37].

Fig. 7: Relative moisture absorption (%) in epoxy coupons Vs. time.

Samples immersed in distilled water at 5°C under various levels of compressive stress. After Yaniv and Ishai, reference [38].

Fig. 8: Reduced  $O_2$  permeability in extruded PET films Vs. stress. After

Seymour and Weinhold, reference [39].

Fig. 9: Solubility  $S$  (in %) Vs. non-dimensional  $\sqrt{\text{time}}$  of epoxy samples

immersed in water. Regime "A" - sorption behavior at 75°C. Regime "B" - increased sorption in a sample equilibrated at 75°C, then cooled to 23°C. After Apicella et. al., reference [36].

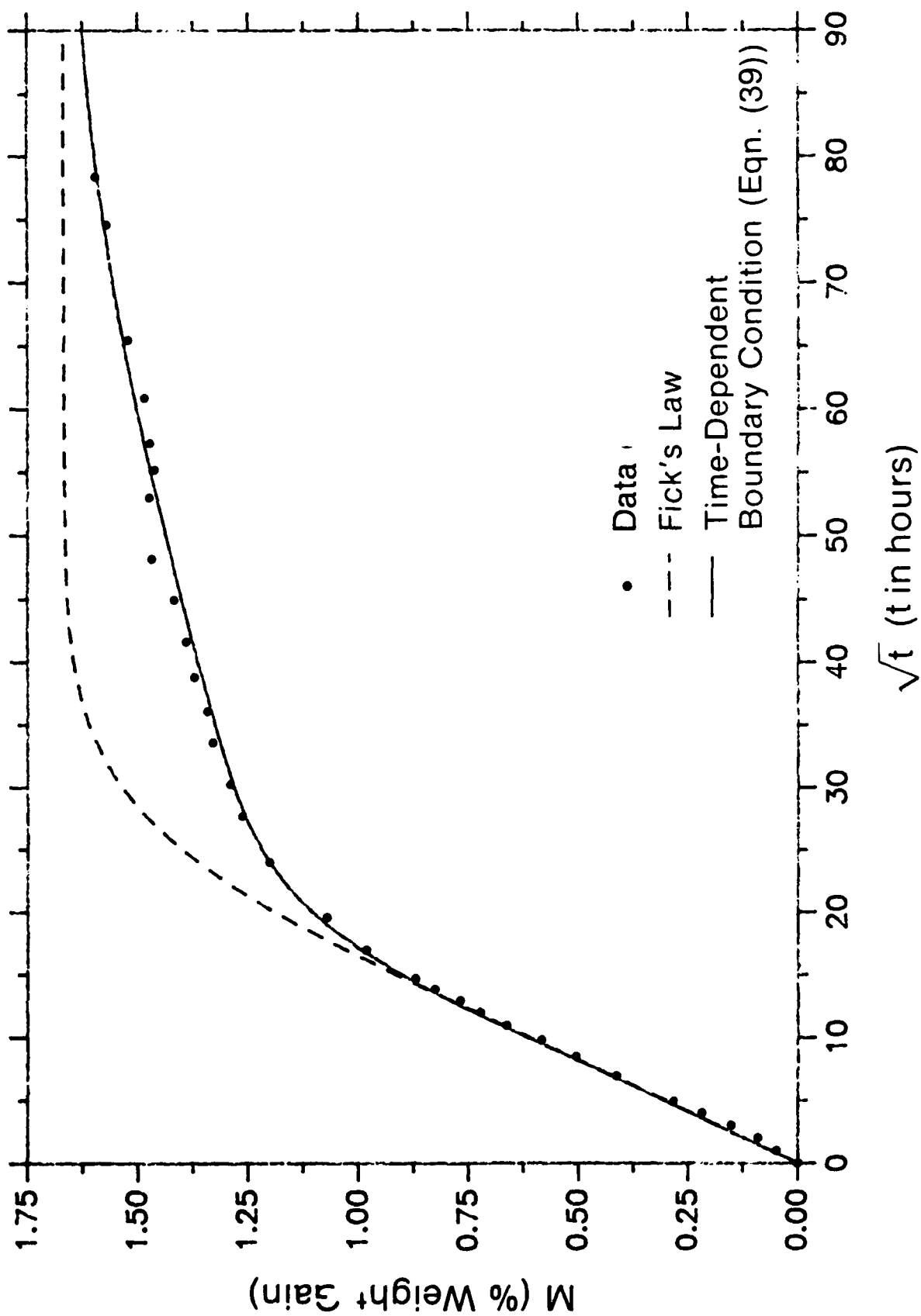


Fig. 1

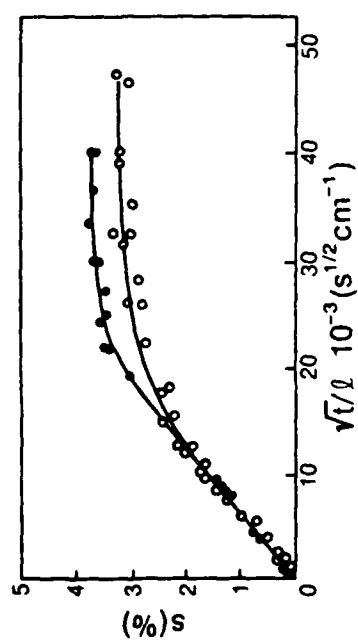


Fig. 2

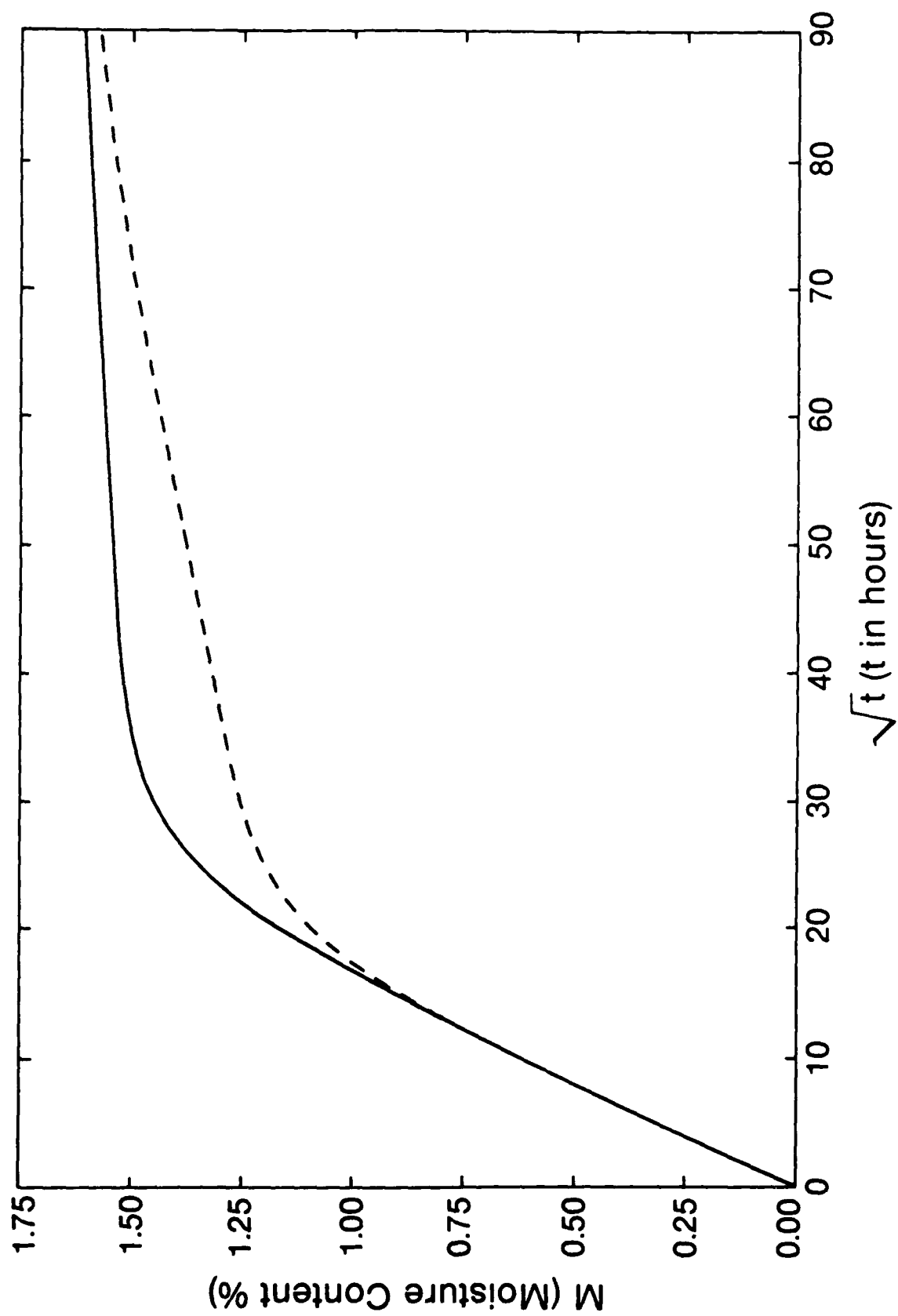


Fig. 3

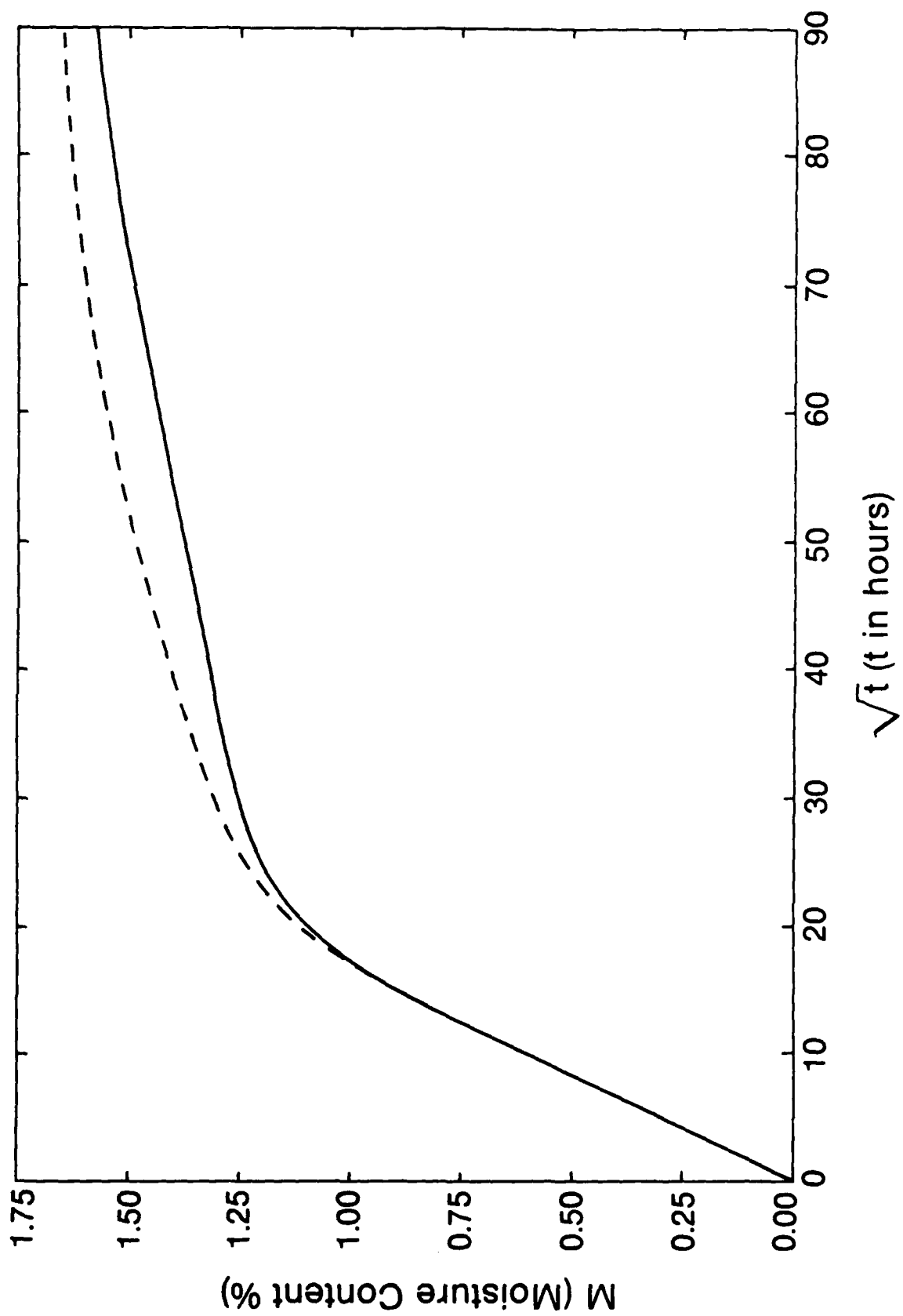


Fig. 4

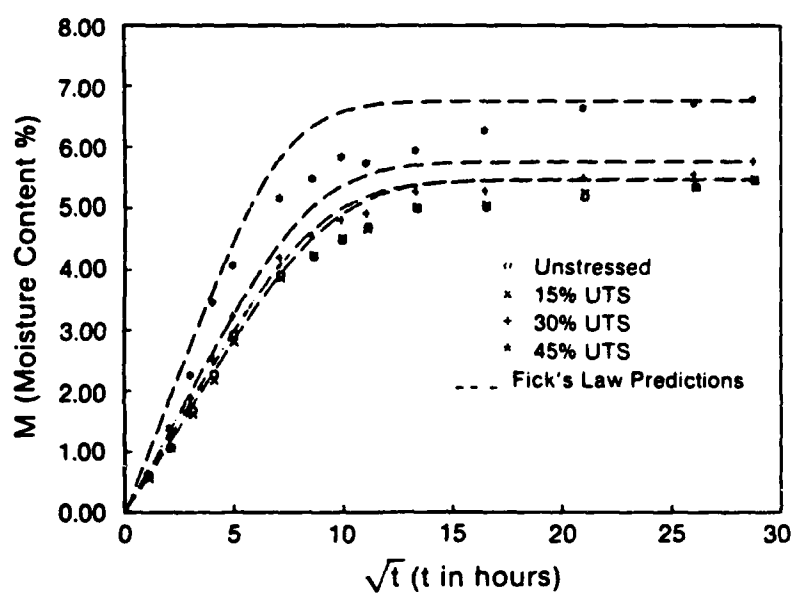


Fig. 5

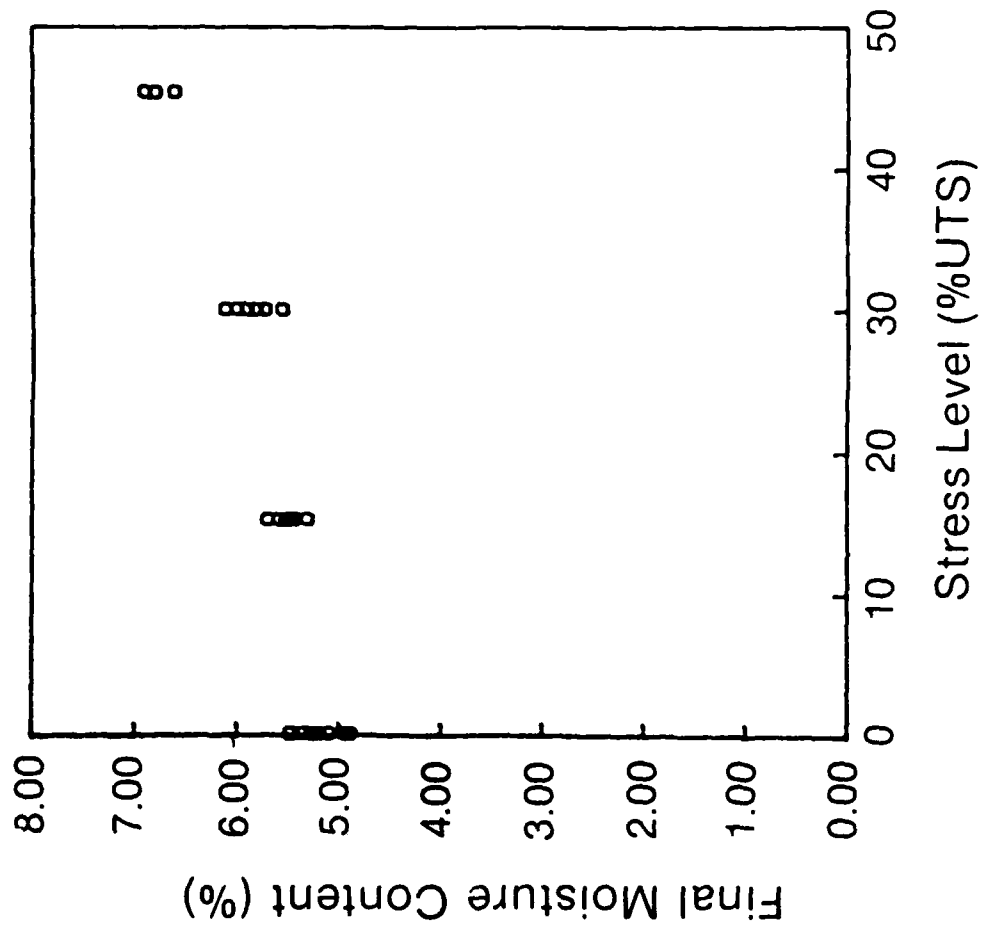


Fig. 6



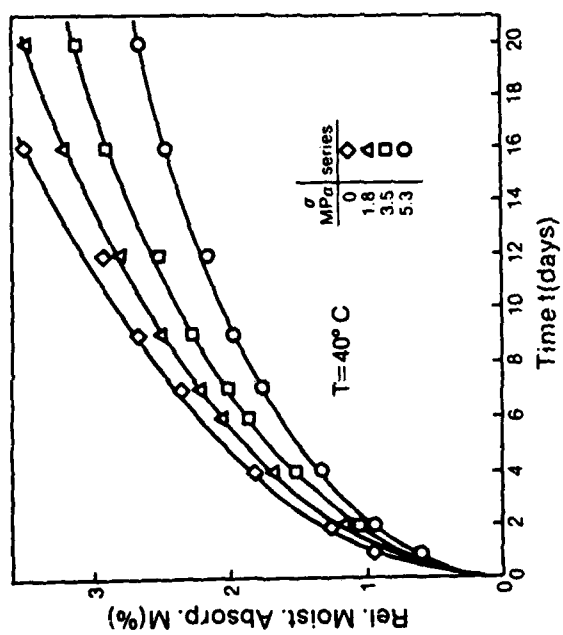


Fig. 7

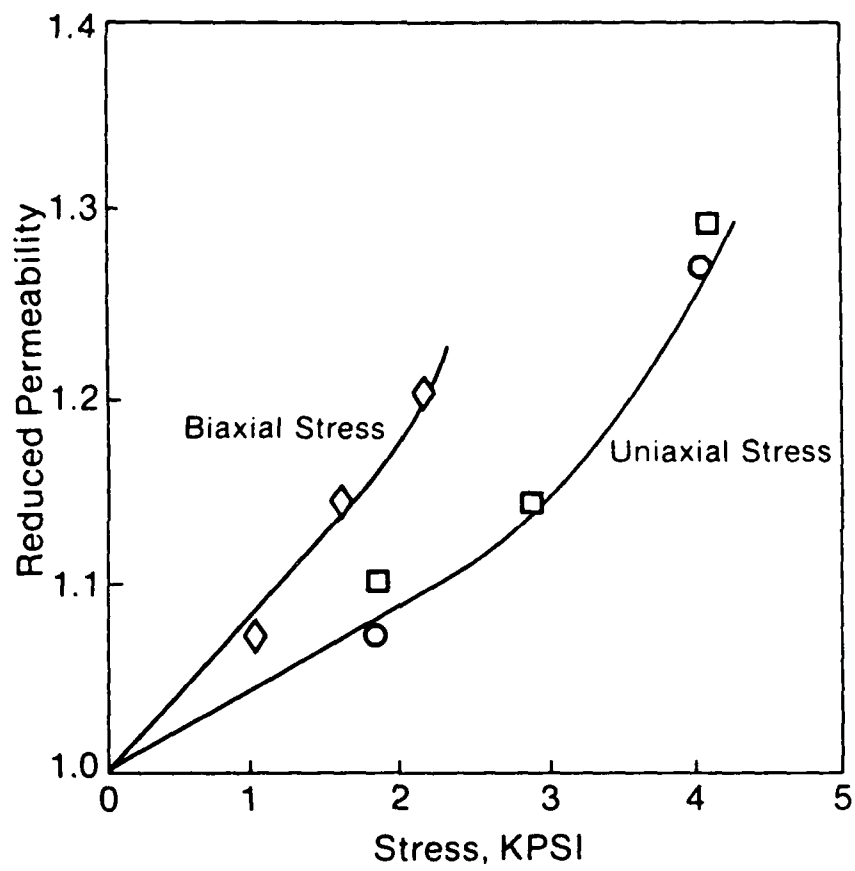


Fig. 8

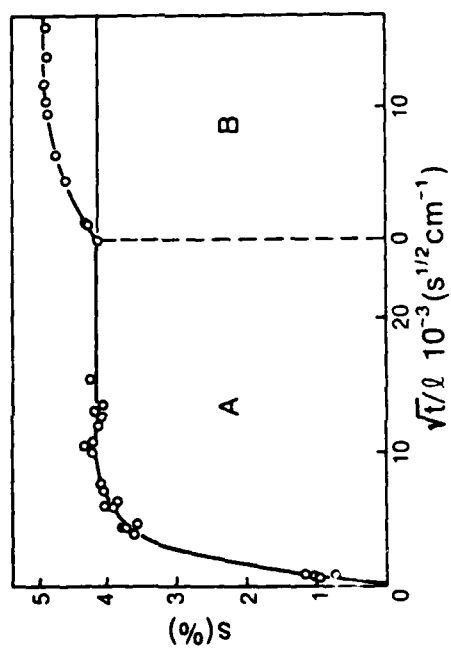


Fig. 9